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<p>(21) International Application Number: PCT/US90/05637</p> <p>(22) International Filing Date: 9 October 1990 (09.10.90)</p> <p>(30) Priority data: 418,832 10 October 1989 (10.10.89) US</p> <p>(60) Parent Application or Grant (63) Related by Continuation US 418,832 (CIP) Filed on 10 October 1989 (10.10.89)</p> <p>(71) Applicant (<i>for all designated States except US</i>): E.I. DU PONT DE NEMOURS AND COMPANY (US/US); 1007 Market Street, Wilmington, DE 19898 (US).</p>		<p>(72) Inventors; and (75) Inventors/Applicants (<i>for US only</i>) : KIELHORN, Fernando, Frederick [US/US]; 303 Weldin Road, Wilmington, DE 19803 (US). MANOGUE, William, Henry [US/US]; 224 Beverly Road, Newark, DE 19711 (US). RAO, V., N., Mallikarjuna [US/US]; 1 Georgetown Avenue, Wilmington, DE 19809 (US).</p> <p>(74) Agents: HEISER, David, E. et al.; E.I. du Pont de Nemours and Company, Legal Department, 1007 Market Street, Wilmington, DE 19898 (US).</p> <p>(81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent), SU, US.</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
<p>(54) Title: HALOCARBON HYDROGENOLYSIS</p> <p>(57) Abstract</p> <p>Halocarbons such as CCl_2F_2, CF_3CFHCl or CF_3CFCl_2 which contain chlorine and/or bromine are contacted with hydrogen in the presence of silicon carbide and/or a metal selected from aluminum, molybdenum, titanium, nickel, iron or cobalt (or their alloys) at temperatures of 350° to 700°C and pressures of 0 to 1000 psig to obtain a product wherein at least one chlorine or bromine in the starting material has been replaced by hydrogen.</p>			

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TITLE

5 HALOCARBON HYDROGENOLYSIS

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of
U.S. application Serial No. 07/418,832 filed
October 10, 1989.

10 BACKGROUND OF THE INVENTION

This invention relates to a process for the
hydrogenolysis of halocarbons.

At this time there is a desire to produce
halocarbons of reduced chlorine content.

15 Hydrogenolysis is a known method for doing this. For
example, see U.K. Patent 1,578,933 which discloses a
process for the hydrogenolysis of CF_3CFHCl to CF_3CH_2F
using a hydrogenation catalyst, e.g., palladium
supported on alumina or carbon. Hydrogenolysis of
20 fluorochlorocarbons by passage through empty tubes
made of various materials is also known, e.g.,
U.S. 2,615,926 discloses platinum tubes,
U.S. 2,704,775 discloses nickel or stainless steel
tubes and U.S. 3,042,727 discloses a Vycor® tube.

25 It is desired to provide a process for
converting a halocarbon to a more hydrogenated form
with high selectivity and particularly to provide
such a process wherein formation of solids and
plugging of reaction vessels is minimized.

30 SUMMARY OF THE INVENTION

We have discovered an improved hydrogenolysis
process for reducing the chlorine and/or bromine
content of halocarbons. The process may be used for
producing saturated halocarbon products such that the
35 yield loss to olefins, coupled by-products,

hydrocarbons or fragmented products is less than 10%. The process involves contacting a halocarbon of 5 the formula:



wherein X is Cl or Br,

n is 1 to 10,

m is 0 to 20,

10 p is 0 to 21,

q is 1 to 22, provided that m+p+q equals 2n+2 when the compound is acyclic and equals 2n when the compound is cyclic, and provided that when n is 1, q is at least 2, with at least 0.1 mole of hydrogen per mole of halocarbon at a temperature of 350° to 700°C, 15 and a pressure of 0 to 1000 psig, in a reaction vessel (e.g., a tube) of aluminum, molybdenum, titanium, nickel, iron, cobalt, or their alloys, or of silicon carbide, optionally packed with aluminum, molybdenum, titanium, nickel, iron, cobalt or their 20 alloys, or an inert material (e.g., silicon carbide) for a time sufficient to produce a product wherein at least one of X has been replaced by a hydrogen atom. Preferred alloys consist essentially of one or more 25 metals selected from aluminum, molybdenum, titanium, nickel, iron and cobalt, optionally together with chromium and/or tungsten.

The process of the invention provides improved 30 conversions and selectivity and has the further advantage that it does not produce olefins as the major product. Furthermore, the process minimizes the formation of solids in the reaction vessel, thus permitting long-term operation with less plugging.

DESCRIPTION OF THE INVENTION

35 An important aspect of the present invention is conducting the hydrogenolysis of halocarbons in the

presence of silicon carbide and/or at least one metal selected from aluminum, molybdenum, titanium, nickel, 5 iron, cobalt or their alloys. The metals may be coated on the inside surface of a reaction vessel (e.g., by plating or sputtering the metals or their alloys onto the inside surface). Such coating can help to minimize corrosion of the reaction vessel 10 well. A reaction vessel of these materials (e.g., a metal tube) optionally packed with the metal in suitable form or an inert material such as silica, silicon carbide or low surface area carbon (e.g., shot coke) may also be used. When reference is made 15 to alloys, it is meant a nickel alloy containing from 1 to 99.9% (by weight) nickel, a cobalt alloy containing 1 to 99.9% (by weight) cobalt, an iron alloy containing 0.2 to 99.9% (by weight) iron, a molybdenum alloy containing 70 to 99.9% (by weight) 20 molybdenum, an aluminum alloy containing 80 to 99.9% (by weight) aluminum and a titanium alloy containing 72 to 99.8% (by weight) titanium. Preferably the remainder of these alloys is selected such that the alloy consists essentially of (i) one or more metals 25 selected from aluminum, molybdenum, titanium, nickel, iron and cobalt, and optionally (ii) chromium and/or tungsten.

Most preferred for the practice of this invention are nickel or alloys of nickel such as 30 those containing 52% to 80% nickel, e.g., Inconel® 600 nickel alloy or Hastelloy® C276 alloy.

When used for packing, the metal, alloys or inert material may be particles or formed shapes such as, for example, perforated plates, saddles, rings 35 (e.g., Pall® rings), wire, screen, chips, pipe, shot, gauze and wool. Although an empty reaction vessel

(e.g., an empty tube) may be used, the use of this type of packing material can provide the advantage of minimizing backmixing. These types of packing material can also serve as heat transfer materials. In many embodiments, perforated plates, saddles and rings can be especially useful.

The invention is applicable to the hydro-
genolysis of halocarbons. The halocarbons can contain 1 to 10 carbon atoms, preferably 1 to 4 carbon atoms, most preferably 1 to 3 carbon atoms. The halocarbons include cyclic as well as acyclic compounds and can be generically represented by the empirical formula $C_nH_mF_pX_q$, where X is Cl and/or Br, preferably Cl, and n is an integer from 1 to 10, m is an integer from 0 to 20, p is an integer from 0 to 21, and q is an integer from 1 to 22, provided that $m+p+q = 2n+2$ when the compound is acyclic and equals 2n when the compound is cyclic. For single carbon compounds (i.e., n is 1) the invention is particularly applicable when q is at least 2.

In a preferred embodiment the halocarbons are represented by the above empirical formula where n = 1 to 4, m is 0 to 8, p is 0 to 9, and q is 1 to 9. Preferably, when n is 2 or more, p is at least 1.

The above halocarbons are either commercially available or can be prepared by known methods or adaptation of known methods.

As previously indicated these starting materials when subjected to the process of the invention will result in products wherein one or more X (e.g., chlorine) has been replaced by hydrogen. Thus the products of the hydrogenolysis reactions of the C_1 halocarbons will contain one or two hydrogen atoms, preferably one, and those from C_2 compounds

from one to three hydrogen atoms, preferably one to two. The C₃ halocarbons hydrogenolysis products will 5 contain one to five hydrogen atoms with those containing one to four being preferred. In a similar manner the C₄ to C₁₀ halocarbon products will contain one or more hydrogen atoms. The preferred process of 10 this invention does not produce olefins as the major product. Instead, the major product of the conversion is a hydrogenolysis product wherein at least one X of the halocarbon starting material has 15 been replaced by a hydrogen atom. This is particularly important for the hydrogenolysis of halocarbons where n is 2 to 10 (i.e., mult carbon 20 halocarbons) where such factors as olefin production can be of concern at temperatures of 350°C or more. For example, CF₃CCl₂F can be converted with high selectivity to a hydrogenolysis product consisting 25 primarily of CF₃CHClF and CF₃CH₂F with very little olefin formulation. In a preferred embodiment of this invention using halocarbons containing fluorine and chlorine, at least 90% of the hydrogenolysis products contain the same number of fluorines as the 30 original halocarbon. Furthermore the yield loss to olefins, coupled by-products, hydrocarbons, fragmentation products or carbon is less than 10%.

Examples of olefins are products such as 35 CC₁F=CCF₂ or CF₂=CF₂ the former of which can be obtained from hydrogenolysis of CC₁₂FCClF₂ and the latter from hydrogenolysis of CC₁F₂CClF₂. An example of a coupled by-product is CF₃CF=CF₃ which can be obtained by the hydrogenolysis of CC₁F₂CClF₂. Examples of hydrocarbon products are CH₄, C₂H₆ and 35 C₃H₈ which can be obtained by the hydrogenolysis of CC₁₂F₂, CC₁₂FCClF₂ and CF₃CClFCF₃ respectively.

Examples of fragmentation products are CF_3H and CH_2F_2 which can be obtained by the hydrogenolysis of

5 $\text{CF}_3\text{CCl}_2\text{F}$ and its isomer.

The reaction temperature can range from 350°C to 700°C. Preferably the reaction temperature is at least about 400°C.

10 The amount of hydrogen contained in the gas stream contacted with the gaseous halocarbon should be at least 0.1 mole per mole of halocarbon. Hydrogen amounts ranging from 0.2 to 5 moles per mole of halocarbon are used for some embodiments. In general, the amount of hydrogen preferably ranges 15 from 0.2 to 60 moles per mole of halocarbon and more preferably ranges from 0.4 to 40 moles per mole of halocarbon. The hydrogen can be fed either in the pure state or diluted with an inert gas, e.g., nitrogen, helium, or argon.

20 The process pressure is operable over a broad range of pressures. Generally atmospheric (i.e., 0 psig) or superatmospheric pressures of up to 1000 psig are employed. Preferably the pressure is at least about 25 psig.

25 The extent of the replacement of halogen by hydrogen increases with reaction time. Reaction times between 0.1 minutes and 25 minutes are preferred. Most preferred are reaction times between 0.2 and 8 minutes.

30 An important feature of the process of the invention is that through selection of the appropriate metal and process conditions, a desired halocarbon hydrogenolysis product can be obtained as the major product with high selectivity and minimal 35 formation of unwanted by-products. Preferably the reaction time and temperature are selected to obtain

long term (>1000 hours) plug free operation and to provide as the major product of the conversion 5 hydrogenolysis product which retains the fluorine content of the starting halocarbon while at least one X is replaced by hydrogen. In many embodiments the reaction time and temperature are controlled so that at least about 90% of halocarbon converted has the 10 same number of fluorine atoms as the halocarbon starting material. Also, in many embodiments the combined yield losses to olefins, coupled by-products, hydrocarbons, or fragmentation products is less than 10%.

15 An additional desirable feature is that through a selection of an appropriate reaction vessel and packing (e.g., metals, alloys, or inert materials) and process conditions, the products of the hydrogenolysis can contain in high selectivity just 20 one less chlorine or bromine than was present in the starting material. This is particularly useful when q is 2 or more, and it is desired to obtain a major product of the conversion, hydrogenolysis product 25 which contains chlorine and/or bromine. For example, starting with a one-carbon compound containing two or more chlorine or bromine atoms, products containing just one less chlorine or bromine can be obtained in high selectivity.

30 Although substantial conversions can be achieved in a once-through system, recycle of unreacted halocarbons or intermediates can be employed in a conventional manner. The processes of this invention are considered to be characterized by 35 relatively high activation energies when compared to catalytic hydrogenolysis over conventional Pd/C catalyst. For example, the activation energy for the

hydrogenolysis of $\text{CF}_3\text{CCl}_2\text{F}$ over a 0.5% Pd/C catalyst at 167°C to 200°C was found to be 14-17 Kcal/mole.

5 The activation energy for the hydrogenolysis of CF_3CHClF over a 0.5% Pd/C catalyst at 249°C to 288°C was found to be 22-28 Kcal/mole. In contrast, the activation energies for the hydrogenolysis reactions of these compounds conducted in the reaction vessels 10 of this invention, either empty or packed, were found to be considerably larger as exemplified in Table A.

15

TABLE A
Activation Energy Data
High Temperature Hydrogenolysis

	<u>Feed</u>	<u>Temp.</u> <u>Range</u>	<u>Packing</u>	<u>Activation</u> <u>Energy</u>
20	F114_a^1	450-550°C	-	49 ± 3 Kcal/mole
	F114_x^2	440-600°C	-	47 ± 2
	F124^3	510-600°C	-	49 ± 7
	F114_x	400-570°C	shot coke	35 ± 1
	F114_x	400-500°C	nickel screen	34 ± 3
	F124	510-570°C	Inconel® screen	41 ± 3
	F124	520-580°C	shot coke	37 ± 1

¹ $\text{F114}_a = \text{CF}_3\text{CCl}_2\text{F}$

² $\text{F114}_x = \text{Du Pont commercial CCIF}_2\text{CClF}_2$ containing some $\text{CF}_3\text{CCl}_2\text{F}$

³ $\text{F124} = \text{CF}_3\text{CHClF}$

30 The products of the reaction can be separated and purified by conventional means. The products can be used as solvents, blowing agents, refrigerants and propellants.

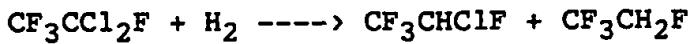
Practice of the invention will become further apparent from the following non-limiting examples.

5 In the following Examples the following general procedure was employed, unless otherwise indicated.

General Procedure - A flow reactor under microprocessor control was used. The reactor, unless otherwise indicated, was a 15" x 1/4" o.d. or 3/8" 10 o.d. Inconel® 600 nickel alloy tube or a 15" x 3/8" Hastelloy® C276 nickel alloy tube bent into a U shape and immersed in a heated fluidized sand bath for temperature control. Inconel® 600 is a commercial alloy containing 76% nickel, 15.5% chromium and 8% 15 iron. Hastelloy® C-276 is a commercial alloy containing 59% nickel, 15.5% chromium, 16% molybdenum and 3.75% tungsten.

The reactor was used either empty or filled with various packing materials as described in the 20 Examples. Hydrogen gas was metered into the system through mass flow controllers. Liquid halocarbons were fed from a syringe pump and vaporized before entering the reactor. Conversions and yields were measured by taking gas stream samples into a gas 25 chromatograph. Product identification was by gc retention times with confirmation by gc-mass spectrometer analysis of samples.

EXAMPLE 1



30 2,2-Dichloro-1,1,1,2-tetrafluoroethane (1.47 g/hr) and hydrogen (molar ratio of H₂/CF₃CCl₂F = 1.9) were fed into the 1/4" empty Inconel® nickel alloy reactor for 38 hours at 450°-550°C and 250 psig. A sample taken after 14 hours at 550°C showed 35 an 89% conversion of CF₃CCl₂F with a 65% selectivity to CF₃CHClF and a 32% selectivity to CF₃CH₂F. Overall selectivity to the two products was 97%.

EXAMPLE 2

5 $\text{CF}_3\text{CCl}_2\text{F} + \text{H}_2 \longrightarrow \text{CF}_3\text{CHClF} + \text{CF}_3\text{CH}_2\text{F}$
2,2-Dichloro-1,1,1,2-tetrafluoroethane
(1.47 g/hr) and hydrogen (molar ratio of $\text{H}_2/\text{CF}_3\text{CCl}_2\text{F} = 1.9$) were fed into the 1/4" empty Inconel® nickel alloy reactor for 132 hours at 350°-550°C and 250 psig. At 350°C a 2.3% conversion of $\text{CF}_3\text{CCl}_2\text{F}$ with a 10 76% selectivity to CF_3CHClF and $\text{CF}_3\text{CH}_2\text{F}$ was observed. A sample taken after 20 hours at 500°C showed an 83% conversion of $\text{CF}_3\text{CCl}_2\text{F}$ with a 98% selectivity to CF_3CHClF and $\text{CF}_3\text{CH}_2\text{F}$.

EXAMPLE 3

15 $\text{CF}_3\text{CHClF} + \text{H}_2 \longrightarrow \text{CF}_3\text{CH}_2\text{F}$
2-Chloro-1,1,1,2-tetrafluoroethane (1.0 g/hr) and hydrogen (molar ratio of $\text{H}_2/\text{CF}_3\text{CHClF} = 4.9$) were fed into the 1/4" empty Inconel® nickel alloy reactor for 7 hours at 550°C and 250 psig with average 20 $\text{CF}_3\text{CH}_2\text{F}$ conversions of 86% with 98% selectivity to $\text{CF}_3\text{CH}_2\text{F}$ and 0.4% selectivity to CF_3CH_3 .

EXAMPLE 4

19 $\text{CF}_2\text{Cl}_2 + \text{H}_2 \longrightarrow \text{CF}_2\text{HCl}$
Dichlorodifluoromethane (9.0 g/hr) and hydrogen (molar ratio of $\text{H}_2/\text{CF}_2\text{Cl}_2 = 1.0$) were fed into the 25 1/4" empty Inconel® nickel alloy reactor as described above for 89 hours at 300 psig, including 79 hours at 500-550°C. For 12 hours at 500°C during this run, at a mean age of 64 synthesis hours, the average 30 conversion of CF_2Cl_2 was 26% with a 97% selectivity to CF_2HCl and a 3% selectivity to CH_2F_2 .

EXAMPLE 5

24 $\text{CF}_3\text{CClFCF}_3 + \text{H}_2 \longrightarrow \text{CF}_3\text{CHFCF}_3$
2-Chloroheptafluoropropane (1.5 g/hr) and 35 hydrogen (22 cc/min) were fed into the 1/4" empty

Inconel® nickel alloy reactor for 3 hours at 450°C and 250 psig with 30-40% conversion and a 98%
5 selectivity to $\text{CF}_3\text{CHFCF}_3$.

EXAMPLE 6

$\text{CF}_3\text{CClFCF}_3 + \text{H}_2 \longrightarrow \text{CF}_3\text{CHFCF}_3$
2-Chloroheptafluoropropane (1.38 g/hr) and
10 hydrogen (22 cc/min) were fed into the 1/4" Inconel®
nickel alloy reactor filled with Inconel® nickel
alloy chips (10 g). Operation at 500°C and 250 psig
for 33.3 hours gave an average of 91.3% conversion
with 99.4% selectivity to $\text{CF}_3\text{CHFCF}_3$.

EXAMPLE 7

15 $\text{CF}_3\text{CCl}_2\text{F} + \text{H}_2 \longrightarrow \text{CF}_3\text{CHClF} + \text{CF}_3\text{CH}_2\text{F}$
2,2-Dichloro-1,1,1,2-tetrafluoroethane (2.9 or
5.9 g/hr) and hydrogen (molar ratio of $\text{H}_2/\text{CF}_3\text{CCl}_2\text{F} =$
2.2 or 4.3) were fed into the 3/8" Inconel® nickel
alloy reactor filled with Inconel® nickel alloy wool
20 (7.96 g) for 106 hours at 400-500°C and 250 psig.
The average conversion of $\text{CF}_3\text{CCl}_2\text{F}$ over the whole
period was 99.9%. For a 12-hour period at 450°C with
a $\text{CF}_3\text{CCl}_2\text{F}$ feed rate of 5.9 g/hr (molar ratio
25 $\text{H}_2/\text{CF}_3\text{CCl}_2\text{F} = 4.3$) the following average
 $\text{CF}_3\text{CH}_2\text{F}$.
selectivities were observed: 69% CF_3CHClF and 26%

EXAMPLE 8

$\text{CF}_3\text{CHClF} + \text{H}_2 \longrightarrow \text{CF}_3\text{CH}_2\text{F}$
2-Chloro-1,1,1,2-tetrafluoroethane (5.5 g/hr)
30 and hydrogen (molar ratio of $\text{H}_2/\text{CF}_3\text{CHClF} = 1.1$) were
fed into the 3/8" Inconel® nickel alloy reactor
filled with a pure nickel screen (8.77 g), operated
at various feed rates and a pressure of 300 psig.
With a CF_3CHClF feed rate of 5.48 g/hr and hydrogen
35 (molar ratio of $\text{H}_2/\text{CF}_3\text{CHClF} = 1.1$) conversion at
525°C and an average synthesis time of 82 hours

averaged 47% with 98% selectivity to $\text{CF}_3\text{CH}_2\text{F}$ for 12 hours. At an average synthesis time of 644 hours 5 conversion averaged 39% with 97% selectivity to $\text{CF}_3\text{CH}_2\text{F}$. At 1181 synthesis hours the operating pressure was increased to 500 psig. Conversion of CF_3CHClF averaged 68% for 14 hours with a selectivity to $\text{CF}_3\text{CH}_2\text{F}$ of 98%.

10

EXAMPLE 9

$\text{CF}_3\text{CHClF} + \text{H}_2 \longrightarrow \text{CF}_3\text{CH}_2\text{F}$
2-Chloro-1,1,1,2-tetrafluoroethane (2.7 or 5.5 g/hr) and hydrogen (molar ratio of $\text{H}_2/\text{CF}_3\text{CHClF} = 1.9$) were fed into the 3/8" Inconel® nickel alloy 15 reactor filled with Inconel® nickel alloy wool (7.96 g) for 23 hours at 400-500°C and 250 psig. Between 18 and 23 hours, at 400°C with a CF_3CHClF feed rate of 2.7 g/hr, the average conversion was 23% and the selectivity to $\text{CF}_3\text{CH}_2\text{F}$ was 82%.

20

EXAMPLE 10

$\text{CF}_2\text{Cl}_2 + \text{H}_2 \longrightarrow \text{CF}_2\text{HCl}$
Dichlorodifluoromethane (4.5 or 33.0 g/hr) and 25 hydrogen (molar ratio of $\text{H}_2/\text{CF}_2\text{Cl}_2 = 1$ or 0.5) were fed into the 3/8" Inconel® nickel alloy reactor filled with pure nickel screen (17.5 g) for 135 hours at 300 psig. For 12 hours at 450° during this run, at a mean synthesis time of 78 hours, with a CF_2Cl_2 feed rate of 4.5 g/hr (molar ratio $\text{H}_2/\text{CF}_2\text{Cl}_2 = 1.0$), the average conversion of CF_2Cl_2 was 34% with the 30 following average selectivities: 95% CF_2HCl and 2.9% CF_2H_2 .

EXAMPLE 11

$\text{CF}_3\text{CClF}_2 + \text{H}_2 \longrightarrow \text{CF}_3\text{CHF}_2$
Chloropentafluoroethane vapor (6 cc/min) and 35 hydrogen (5 cc/min) were fed into a Hastelloy® nickel alloy reactor (6" x 1/2" O.D.) filled with pure

nickel screen (39.68 g) at 550°C and atmospheric pressure. The reaction products were analyzed with 5 the following results: 59% conversion of CF_3CClF_2 with a 97% selectivity to CF_3CHF_2 .

EXAMPLE 12

$\text{CF}_3\text{CClF}_2 + \text{H}_2 \longrightarrow \text{CF}_3\text{CHF}_2$
Chloropentafluoroethane vapor (5 cc/min) and 10 hydrogen (6 cc/min) were fed into an Inconel® nickel alloy reactor (6" x 1/2" O.D.) filled with pure nickel screen (51.98 g) at 550°C and atmospheric pressure. The reaction products were analyzed with 15 the following results: 65% conversion of CF_3CClF_2 with a 95% selectivity to CF_3CHF_2 .

The reaction was run under the same conditions as described above, except that the feed rates were changed to CF_3CClF_2 (5 cc/min) and H_2 (12 cc/min). The reaction products were analyzed with the 20 following results: 62% conversion of CF_3CClF_2 with an 86% selectivity to CF_3CHF_2 .

EXAMPLE 13

$\text{CClF}_2\text{CClF}_2/\text{CF}_3\text{CCl}_2\text{F} + \text{H}_2 \longrightarrow$
 $\text{CHF}_2\text{CClF}_2/\text{CF}_3\text{CHClF} + \text{CHF}_2\text{CHF}_2/\text{CF}_3\text{CH}_2\text{F}$
25 A vapor mixture of $\text{CClF}_2\text{CClF}_2$ (9)/ $\text{CF}_3\text{CCl}_2\text{F}$ (1) (5 cc/min) and hydrogen (6 cc/min) was fed into a Hastelloy® nickel alloy reactor (6" x 1/2" O.D.) filled with pure nickel screen (39.68 g) at 550°C and atmospheric pressure. The reaction products were 30 analyzed with the following results: 61% conversion of $\text{CClF}_2\text{CClF}_2/\text{CF}_3\text{CCl}_2\text{F}$ with a 46% selectivity to $\text{CHF}_2\text{CClF}_2/\text{CF}_3\text{CHClF}$ and a 34% selectivity to $\text{CHF}_2\text{CHF}_2/\text{CF}_3\text{CH}_2\text{F}$.

EXAMPLE 14

5 $\text{CF}_3\text{CCl}_2\text{F} + \text{H}_2 \longrightarrow \text{CF}_3\text{CHClF} + \text{CF}_3\text{CH}_2\text{F}$
2,2-Dichlorotetrafluoroethane vapor (5 cc/min)
and hydrogen (6 cc/min) were fed into an Inconel®
nickel alloy reactor (6" x 1/2" O.D.) filled with
pure nickel screen (51.98 g) at 550°C and atmospheric
pressure. The reaction products were analyzed with
10 the following results: 83% conversion of $\text{CF}_3\text{CCl}_2\text{F}$
with a 5% selectivity to CF_3CHClF and a 66%
selectivity to $\text{CF}_3\text{CH}_2\text{F}$.

EXAMPLE 15

15 $\text{CF}_3\text{CHClF} + \text{H}_2 \longrightarrow \text{CF}_3\text{CH}_2\text{F}$
2-Chloro-1,1,1,2-tetrafluoroethane vapor (5
cc/min) and hydrogen (6 cc/min) were fed into an
Inconel® nickel alloy reactor (6" x 1/2" O.D.) filled
with pure nickel screen (51.98 g) at 550°C and
atmospheric pressure. The reaction products were
20 analyzed with the following results: 58% conversion
of CF_3CHClF with an 85% selectivity to $\text{CF}_3\text{CH}_2\text{F}$.

EXAMPLE 16

25 $\text{CCl}_2\text{CCl}_2\text{F} + \text{H}_2 \longrightarrow \text{CHClFCClF}_2 + \text{CHClFCHF}_2$
1,1,2-Trichloro-1,2,2-trifluoroethane
(3.13 g/hr) and hydrogen (molar ratio = 4.75) were
fed into the 3/8" Inconel® nickel alloy U-tube
reactor as described in the general procedure, with
the exit leg filled with pure nickel screen (8 g), at
450°C and 500 psig. Over a 6-hour period the
30 reaction products were analyzed with the following
results: 81% conversion of $\text{CCl}_2\text{CCl}_2\text{F}$ with 96%
combined selectivity to $\text{C}_2\text{H}_3\text{F}_3$, $\text{C}_2\text{H}_2\text{ClF}_3$, and
 $\text{C}_2\text{HCl}_2\text{F}_3$. Selectivity to $\text{CClF} = \text{CF}_2$ was 2%. When
the temperature was raised to 475°C for 7 hours, the
35 average conversion of $\text{CCl}_2\text{CCl}_2\text{F}$ was 97% with 95%
combined selectivity to $\text{C}_2\text{H}_3\text{F}_3$, $\text{C}_2\text{H}_2\text{ClF}_3$, and
 $\text{C}_2\text{HCl}_2\text{F}_3$. Selectivity to $\text{CClF} = \text{CF}_2$ was 1%.

EXAMPLE 17

5 $\text{CF}_3\text{CHClF} + \text{H}_2 \longrightarrow \text{CF}_3\text{CH}_2\text{F}$
2-Chloro-1,1,1,2-tetrafluoroethane (2.7 g/hr) and hydrogen (molar ratio of $\text{H}_2/\text{CF}_3\text{CHClF} = 0.2$) were fed into an empty 6" x 1/2" O.D. Hastelloy® C276 nickel alloy reactor for 8 hours at 535°C and 300 psig. The average conversion of CF_3CHClF was 22%
10 with an average 97% $\text{CF}_3\text{CH}_2\text{F}$ selectivity.

EXAMPLE 18

15 $\text{CF}_3\text{CHClF} + \text{H}_2 \longrightarrow \text{CF}_3\text{CH}_2\text{F}$
2-Chloro-1,1,1,2-tetrafluoroethane (2.7 g/hr) and hydrogen (molar ratio of $\text{H}_2/\text{CF}_3\text{CHClF} = 1.5$) were fed into 6" x 1/2" O.D. Hastelloy® C276 nickel alloy reactor containing 14/20 mesh acid-washed SiC (6.5 g) for 60 hours at 535°C and 300 psig. The average conversion of CF_3CHClF was 75% with an average 97% $\text{CF}_3\text{CH}_2\text{F}$ selectivity.

20 EXAMPLE 19

18 $\text{CF}_3\text{CHClF} + \text{H}_2 \longrightarrow \text{CF}_3\text{CH}_2\text{F}$
2-Chloro-1,1,1,2-tetrafluoroethane and hydrogen were fed at various rates over 113 hours into the 3/8" Hastelloy® C276 nickel alloy tube operated at 300 psig and containing Conoco Shot coke (9.2 grams, 10 cc), a highly fused petroleum coke with a surface area of 0.5 sq m/g. For an 8-hour period at 560°C and an average time in synthesis of 102 hours, with a CF_3CHClF feed rate of 11.0 g/hr and a hydrogen feed rate of 32 cc/min (molar ratio of $\text{H}_2/\text{CF}_3\text{CHClF} = 1$) the average conversion of CF_3CHClF was 13% with an average selectivity to $\text{CF}_3\text{CH}_2\text{F}$ of 99%.

EXAMPLE 20

35 $\text{CClF}_2\text{CClF}_2 + \text{H}_2 \longrightarrow \text{CHF}_2\text{CClF}_2 + \text{CHF}_2\text{CHF}_2$
Commercial 1,2-dichloro-1,1,2,2-tetrafluoroethane, containing 9% (molar) 1,1-dichloro-1,2,2,2-

5 tetrafluoroethane, and hydrogen were fed at various rates over 150 hours into the 3/8" Inconel® nickel alloy tube operated at 300 psig and containing Conoco Shot coke (9.2 grams, 10 cc), a highly fused petroleum coke with a surface area of 0.5 sq. m/g. For a 16-hour period at 550°C and an average time in synthesis of 59 hours, with a $\text{CClF}_2\text{CClF}_2$ feed rate of 10 5.9 g/hr and a hydrogen feed rate of 28 cc/min (molar ratio of $\text{H}_2/\text{CClF}_2\text{CClF}_2 = 2$) the average conversion of the $\text{C}_2\text{Cl}_2\text{F}_4$ isomers was 84% with an average selectivity to $\text{CHF}_2\text{CClF}_2$ and its isomer of 49%, and an average selectivity to CHF_2CHF_2 and its isomer of 15 47%.

EXAMPLE 21

$\text{CF}_3\text{CCl}_2\text{F} + \text{H}_2 \longrightarrow \text{CF}_3\text{CHClF} + \text{CF}_3\text{CH}_2\text{F}$
2,2-Dichloro-1,1,1,2-tetrafluoroethane
20 (2 mL/h), which was vaporized before being mixed with hydrogen (13 cc/min), was fed into a Hastelloy® C nickel alloy reactor (6" x 1/2" O.D.) as described above, containing Conoco Shot coke (14.0 grams, 10 mesh), a highly fused petroleum coke with a surface area of 0.5 sq m/g at 550°C and 100 psig. 25 After 28 hours of operation, product analysis indicated that $\text{CF}_3\text{CCl}_2\text{F}$ conversion was quantitative and selectivity to CF_3CHClF and $\text{CF}_3\text{CH}_2\text{F}$ was 64.7% and 33.3% respectively.

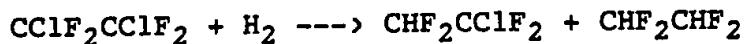
EXAMPLE 22

30 $\text{CF}_3\text{CClF}_2 + \text{H}_2 \longrightarrow \text{CF}_3\text{CHF}_2$
Chloropentafluoroethane vapor (10 cc/min) and hydrogen (10 cc/min) were fed into a Hastelloy® C nickel alloy reactor (6" x 1/2" O.D.) as described above, charged with Conoco Shot coke (14.0 grams, 10 mesh), a highly fused petroleum coke with a surface area of 0.5 sq m/g at 550°C. After 10 hours of

operation, product analysis indicated that CF_3CClF_2 conversion was 7.5% and selectivity to CF_3CHF_2 was 94.7%.

This experiment was substantially repeated except that the CF_3CClF_2 flow was 5 cc/min and the hydrogen flow was 6 cc/min. Product analysis indicated that CF_3CClF_2 conversion was 13.3% and selectivity to CF_3CHF_2 was 89.6%.

EXAMPLE 23



Commercial 1,2-dichloro-1,1,2,2-tetrafluoro-ethane, containing 9% (molar) 1,1-dichloro-1,2,2,2-tetrafluoroethane, and hydrogen were fed at various rates for 172 hours into an empty 15" x 3/8" O.D. Hastelloy® C276 nickel alloy tube, as described above, operated at 500 psig. For a 13 hour period at 500°C and an average time in synthesis of 66 hours, with a $\text{CClF}_2\text{CClF}_2$ feed rate of 5.9 g/hr and hydrogen feed rate of 10 cc/min (molar ratio of $\text{H}_2/\text{CClF}_2\text{CClF}_2 = 0.7$) the average conversion of $\text{C}_2\text{Cl}_2\text{F}_4$ isomers was 58% with an average selectivity to $\text{CHF}_2\text{CClF}_2$ and its isomer of 75% and an average selectivity to CHF_2CHF_2 and its isomer of 24%. For a 9 hour period at 500°C and an average time in synthesis of 148 hours, with a $\text{CClF}_2\text{CClF}_2$ feed rate of 1.47 g/hr and a molar feed ratio of $\text{H}_2/\text{CClF}_2\text{CClF}_2$ of 1.5 the average conversion of $\text{C}_2\text{Cl}_2\text{F}_4$ isomers was 88% with an average selectivity of $\text{CHF}_2\text{CClF}_2$ and its isomer of 45% and an average selectivity to CHF_2CHF_2 and its isomer of 54%.

EXAMPLE 24

5 $\text{CCl}_2\text{CClF}_2 + \text{H}_2 \longrightarrow \text{CHF}_2\text{CClF}_2 + \text{CHF}_2\text{CHF}_2$
Commercial 1,2-dichloro-1,1,2,2-tetrafluoro-
ethane, containing 9% (molar) 1,1-dichloro-1,2,2,2-
tetrafluoroethane, and hydrogen were fed at various
rates for 192 hours into a 15" x 3/8" O.D. Inconel®
600 nickel alloy tube, as described above, containing
10 8.0 g of 24 x 100 mesh nickel screen and operated at
500 psig. For a 10 hour period at 400°C and a
 $\text{CCl}_2\text{CClF}_2$ feed rate of 0.7 g/hr and hydrogen feed
rate of 1.7 cc/min (molar ratio of $\text{H}_2/\text{CCl}_2\text{CClF}_2 = 1$); the average conversion of $\text{C}_2\text{Cl}_2\text{F}_4$ isomers was 61%
15 with an average selectivity to $\text{CHF}_2\text{CClF}_2$ and its
isomer of 77.0% and an average selectivity to
 CHF_2CHF_2 and its isomer of 22.7%.

EXAMPLE 25

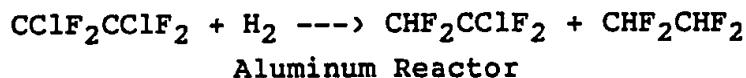
20 $\text{CF}_3\text{CCl}_2\text{F} + \text{H}_2 \longrightarrow \text{CF}_3\text{CHClF} + \text{CF}_3\text{CH}_2\text{F}$
2,2-Dichloro-1,1,1,2-tetrafluoroethane and
hydrogen were fed at various rates for 68 hours to an
empty Hastelloy® C276 nickel alloy tube, as described
above, operated at 500 psig. For a five hour period
25 at 500°C and an average time in synthesis of 41
hours, with a $\text{CF}_3\text{CCl}_2\text{F}$ feed rate of 5.9 g/hr and a
hydrogen rate of 14 cc/min (molar ratio of
 $\text{H}_2/\text{CF}_3\text{CCl}_2\text{F} = 1$), the average conversion was 64% with
an average selectivity to CF_3CHClF of 83.6 and an
30 average selectivity of $\text{CF}_3\text{CH}_2\text{F}$ of 15.6%.

EXAMPLE 26

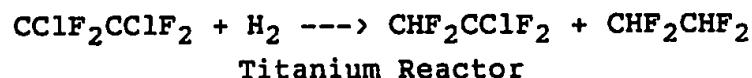
35 $\text{CCl}_2\text{CClF}_2 + \text{H}_2 \longrightarrow \text{CHF}_2\text{CClF}_2 + \text{CHF}_2\text{CHF}_2$
Chrome-Plated Reactor
Commercial 1,2-dichloro-1,1,2,2 tetrafluoro-
ethane, containing 9% (molar) 1,1-dichloro-1,2,2,2

5 tetrafluoroethane, and hydrogen were fed at various
rates over 55 hours into a 15" x 1/4" o.d. empty
10 chrome-plated U-tube reactor, as described above,
operated at 300 psig. For a 20-hour period at 500°C
and an average time in synthesis of 16 hours, with a
CClF₂CClF₂ feed rate of 2.9 g/hr and a hydrogen feed
rate of 13.3 cc/min (molar ratio H₂/CClF₂CClF₂ = 2);
15 the average conversion of the CClF₂CClF₂ isomers was
56% with an average selectivity to CHF₂CClF₂ and its
isomer of 21%, and an average selectivity to CHF₂CHF₂
and its isomer of 76%.

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EXAMPLE 27

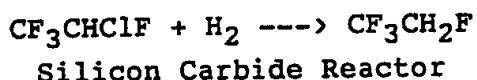
20 Commercial 1,2-dichloro-1,1,2,2,2 tetrafluoro-
ethane, containing 9% (molar) 1,1-dichloro-1,2,2,2
25 tetrafluoroethane, and hydrogen were fed at various
rates over 31 hours into an empty 15" x 1/4" o.d.
aluminum U-tube reactor, as described above, operated
at 50 psig. For a 3-hour period at 500°C and an
average time in synthesis of 28 hours, with a
CClF₂CClF₂ feed rate of 1.47 g/hr and a hydrogen feed
rate of 7.0 cc/min (molar ratio H₂/CClF₂CClF₂ = 2);
30 the average conversion of the CClF₂CClF₂ isomers was
5% with an average selectivity to CHF₂CClF₂ and its
isomer of 49%, and an average selectivity to CHF₂CHF₂
and its isomers of 33%.

EXAMPLE 28

35 Commercial 1,2-dichloro-1,1,2,2,2 tetrafluoro-
ethane, containing 9% (molar) 1,1-dichloro-1,2,2,2-

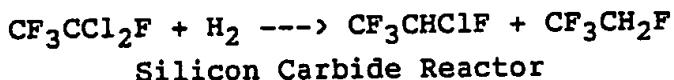
tetrafluoroethane, and hydrogen were fed at various rates over 42 hours into a 15" x 1/4" o.d. empty 5 titanium U-tube reactor, as described above, operated at 50 psig. For a 17-hour period at 500°C and an average time in synthesis of 9.5 hours, with a $\text{CClF}_2\text{CClF}_2$ feed rate of 2.9 g/hr and a hydrogen feed rate of 13.9 cc/min (molar ratio $\text{H}_2/\text{CClF}_2\text{CClF}_2 = 2$) 10 the average conversion of the $\text{CClF}_2\text{CClF}_2$ isomers was 14.2% with an average selectivity to $\text{CHF}_2\text{CClF}_2$ and its isomer of 57%, and an average selectivity to CHF_2CHF_2 and its isomer of 24.4%.

15

EXAMPLE 29

2-Chloro-1,1,1,2 tetrafluoroethane and hydrogen were fed at various rates over 47 hours into a 15" x 20 1/4" o.d. empty silicon carbide straight tube reactor, as described above, operated at 0 psig. For a 12-hour period at 600°C and an average time in synthesis of 29 hours, with a CF_3CHClF feed rate of 2.74 g/hr and a hydrogen feed rate of 8.2 cc/min 25 (molar ratio $\text{H}_2/\text{CF}_3\text{CHClF} = 1$); the average conversion of the CF_3CHClF was 4.3%, with an average selectivity to $\text{CF}_3\text{CH}_2\text{F}$ of 89.7%.

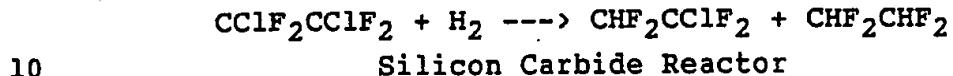
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EXAMPLE 30

2,2-Dichloro-1,1,1,2-tetrafluoroethane 2.94 g/hr were fed into a silicon carbide straight tube reactor, as described above, with 6.4 cc/min of 35 hydrogen (molar ratio $\text{H}_2/\text{CF}_3\text{CCl}_2\text{F} = 1$) operated at 0 psig for 41 hours. Over a 15-hour period at 500°C

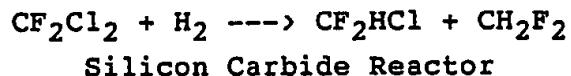
and an average time in synthesis of 27 hours; the
average conversion of $\text{CF}_3\text{CCl}_2\text{F}$ was 23% with an
5 average selectivity to CF_3CHClF of 54% and an average
selectivity to $\text{CF}_3\text{CH}_2\text{F}$ of 0.6%.

EXAMPLE 31



Commercial 1,2-dichloro-1,1,2,2-tetrafluoroethane, containing 9% (molar) 1,1-dichloro-1,2,2,2-tetrafluoroethane, and hydrogen were fed at various feed rates over 38 hours into a straight tube silicon carbide reactor tube, as described above, operated at 0 psig. For a 12-hour period at 575°C and at an average time in synthesis of 14 hours, with a feed rate of 13.9 cc/min of hydrogen and 2 grams/hr of $\text{CClF}_2\text{CClF}_2$ (molar ratio $\text{H}_2/\text{CClF}_2\text{CClF}_2 = 2$); the 20 average conversion of the $\text{CClF}_2\text{CClF}_2$ isomers was 35.6% with an average selectivity to $\text{CHF}_2\text{CClF}_2$ and its isomers of 28% and an average selectivity to CHF_2CHF_2 and its isomers of 27%.

25 EXAMPLE 32



Dichlorodifluoromethane (2.6 g/hr) and hydrogen (molar ratio $\text{H}_2/\text{CF}_2\text{Cl}_2 = 1.0$) were fed into an empty 30 1/2" x 15" silicon carbide straight tube reactor, as described above, over a 28-hour period. For four hours at 575°C during this run, at an average synthesis time of 26 hours; the average conversion of CF_2Cl_2 was 35.6% with an 82% selectivity to CF_2HCl 35 and a 2% selectivity to CH_2F_2 .

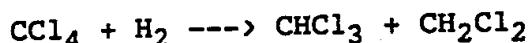
EXAMPLE 33



Hastelloy® Nickel Alloy Reactor

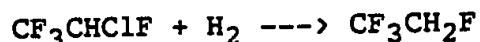
1,1,1-Trichloro-2,2,2-trifluoroethane and hydrogen were fed into an empty 15" x 3/8" Hastelloy® C276 nickel alloy U-tube reactor, as described above, at 300 psig for a period of 28 hours. Over a 6-hour period at 425°C and 300 psig, at an average time in synthesis of 17 hours, with a feed rate of CF_3CCl_3 of 6.25 g/hr and a hydrogen feed rate of 14.0 sccm (molar ratio $\text{H}_2/\text{CF}_3\text{CCl}_3 = 1.0$); the average conversion of CF_3CCl_3 was 33% with a selectivity to CF_3CHCl_2 of 95% and a selectivity to $\text{CF}_3\text{CH}_2\text{Cl}$ of 5%.

EXAMPLE 34



Inconel® Nickel Alloy Reactor

EXAMPLE 35.

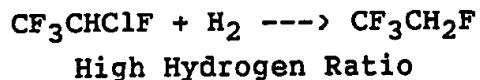


High Hydrogen Ratio

35 2-Chloro-1,1,1,2-tetrafluoroethane and hydrogen
were fed at varying rates for over 48 hours to a 56"

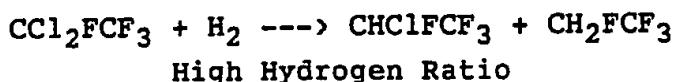
5 x 1/4" Inconel® 600 nickel alloy coil reactor at 300
psig and temperatures between 550 and 600°C. For 4
hours at 600°C, at an average time in synthesis of 39
hours, with a CF_3CHClF feed rate of 1.6 mL/hr and a
10 H_2 feed rate of 130 sccm ($\text{H}_2/\text{CF}_3\text{CHClF}$ mol ratio = 20)
the average conversion of CF_3CHClF was 83% and the
selectivity to $\text{CF}_3\text{CH}_2\text{F}$ was 94%. At a lower H_2 flow
15 of 65 sccm and the same CF_3CHClF feed rate and
temperature ($\text{H}_2/\text{CF}_3\text{CHClF}$ mol ratio = 10) the average
conversion of CF_3CHClF over a 5-hour period was 90%
with a 94% selectivity to $\text{CF}_3\text{CH}_2\text{F}$.

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EXAMPLE 36

20 2-Chloro-1,1,1,2-tetrafluoroethane and hydrogen
were fed at various rates for 1207 hours into a 15" x
3/8" Inconel® 600 nickel alloy U-tube, packed with
8.77 g 150 mesh nickel screen, and operated at
various temperatures at 300 psig. For a 23-hour
period at 550°C and an average time in synthesis of
755 hours with a CF_3CHClF feed rate of 0.4 ml/hour
25 and a hydrogen feed rate of 18 sccm/min (molar ratio
 $\text{H}_2/\text{CF}_3\text{CHClF}$ = 11), the average conversion of CF_3CHClF
was 99.6% with a selectivity to $\text{CF}_3\text{CH}_2\text{F}$ of 93%.

30

EXAMPLE 37

35 1,1-Dichloro-1,2,2,2-tetrafluoroethane and
hydrogen were fed at various rates for 237 hours into
a 15" x 3/8" Hastelloy® C nickel alloy U-tube packed
with 9.29 g of Conoco shot coke and operated at
various temperatures at 300 psig. For a 5-hour

period at 575°C and an average time in synthesis of 227 hours with a CCl_2FCF_3 feed rate of 36 mL/hr and a 5 hydrogen feed rate of 50 sccm/min (molar ratio $\text{H}_2/\text{CCl}_2\text{FCF}_3 = 40$), the average conversion of CCl_2FCF_3 was 100%. The selectivity to CHClFCF_3 was 32% and the selectivity to CH_2FCF_3 was 59%.

10

EXAMPLE 38

$\text{CF}_3\text{CClF}_2 + \text{H}_2 \rightarrow \text{CF}_3\text{CHF}_2$
2-Chloro-1,1,1,2,2-pentafluoroethane and hydrogen were fed at various rates to 15" x 3/8" Hastelloy® C276 nickel alloy U-tube operated at 300 15 psig and various temperatures for 136 hours. For 10 hours, at an average time in synthesis of 58 hours and a temperature of 575°C, with a CF_3CClF_2 feed rate of 2.1 g/hr and a hydrogen feed rate of 14.0 sccm (molar ratio $\text{H}_2/\text{CF}_3\text{CClF}_2 = 2.5$), the conversion of 20 CF_3CClF_2 was 89.5% and the selectivity to CF_3CHF_2 was 99.9%.

For an 8-hour period at an average time in synthesis of 131 hours and a temperature of 575°C, with a feed rate of CF_3CClF_2 of 4.15 g/hr and a 25 hydrogen feed rate of 329 sccm (molar ratio $\text{H}_2/\text{CF}_3\text{CClF}_2 = 30$), the average conversion of CF_3CClF_2 was 39% with a selectivity to CF_3CHF_2 was 99.6%.

Particular embodiments of the invention are 30 included in the examples. Other embodiments will become apparent to those skilled in the art from a consideration of the specification or practice of the invention disclosed herein. It is understood that 35 modifications and variations may be practiced without departing from the spirit and scope of the novel concepts of this invention. It is further understood

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that the invention is not confined to the particular
formulations and examples herein illustrated, but it
5 embraces such modified forms thereof as come within
the scope of the following claims.

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CLAIMS

5 1. A process for the hydrogenolysis of
halocarbons comprising: contacting a halocarbon of
the formula



wherein X is Cl or Br,

10 n is 1 to 10,
m is 0 to 20,
p is 0 to 21,
q is 1 to 22, provided that m+p+q equals 2n+2
when the compound is acyclic and equals 2n when the
15 compound is cyclic, and provided that when n is 1, q
is at least 2, with at least 0.1 mole of hydrogen per
mole of said halocarbon in a reaction vessel of
aluminum, molybdenum, titanium, nickel, iron, cobalt,
or their alloys or of silicon carbide, which is
20 either empty or is packed with particles or formed
shapes of aluminum, molybdenum, titanium, nickel,
iron, cobalt, or their alloys or silicon carbide or
low surface area carbon at a pressure within the
range of from 0 psig to 1000 psig, at a temperature
25 within the range of from 350°C to 700°C and for a
time sufficient to produce a product wherein at least
one of X has been replaced by a hydrogen atom.

30 2. The process of Claim 1 wherein the
temperature ranges from 400°C to 700°C and the
pressure is 0 to 500 psig.

35 3. The process of Claim 1 wherein X is Cl, n
is 1 to 4, m is 0 to 8, p is 0 to 9 and q is 1 to 9.

4. The process of Claim 3 wherein n is 1
to 3.

5. The process of Claim 1 wherein the halocarbon is selected from $\text{CF}_3\text{CCl}_2\text{F}$, CF_3CHClF ,
5 CCl_4 , CCl_2F_2 , $\text{CClF}_2\text{CClF}_2$, $\text{CHF}_2\text{CClF}_2$, $\text{C}_2\text{F}_5\text{Cl}$,
 $\text{CClF}_2\text{CCl}_2\text{F}$, CF_3CCl_3 , $\text{CCl}_2\text{FCCl}_2\text{F}$ or $\text{CClF}_2\text{CCl}_3$.

6. The process of Claim 1 which is conducted in the presence of nickel or a nickel alloy.

10

7. The process of Claim 1 wherein the reaction vessel is packed with silicon carbide or low surface area carbon.

15

8. The process of Claim 1 wherein the ratio of moles of hydrogen to moles of halocarbon ranges from 0.2 to 5.

20

9. The process of Claim 2 wherein the halocarbon is $\text{CClF}_2\text{CClF}_2$, the reaction vessel is nickel or a nickel alloy and is either empty or packed with nickel or a nickel alloy, and the reaction time is between 0.2 and 8 minutes.

25

10. The process of Claim 2 wherein the halocarbon is $\text{CF}_3\text{CCl}_2\text{F}$, the reaction vessel is nickel or a nickel alloy and is either empty or packed with nickel or a nickel alloy, and the reaction time is between 0.2 and 8 minutes.

30

11. The process of Claim 2 wherein the halocarbon is CF_3CHClF , the reaction vessel is nickel or a nickel alloy and is either empty or packed with nickel or a nickel alloy, and the reaction time is between 0.2 and 8 minutes.

35

12. The process of Claim 2 wherein the halocarbon is CF_3CClF_2 , the reaction vessel is nickel or a nickel alloy and is either empty or packed with nickel or a nickel alloy, and the reaction time is between 0.2 and 8 minutes.

13. The process of Claim 2 wherein the halocarbon is CCl_4 , the reaction vessel is nickel or a nickel alloy and is either empty or packed with nickel or a nickel alloy, and the reaction time is between 0.2 and 8 minutes.

15 14. The process of Claim 2 wherein the halocarbon is CF_2Cl_2 , the reaction vessel is nickel or a nickel alloy and is either empty or packed with nickel or a nickel alloy, and the reaction time is between 0.2 and 8 minutes.

20 15. The process of Claim 2 wherein the halocarbon is $CClF_2CHF_2$, the reaction vessel is nickel or a nickel alloy and is either empty or packed with nickel or a nickel alloy, and the reaction time is between 0.2 and 8 minutes.

30 16. The process of Claim 2 wherein the halocarbon is C_3ClF_7 isomer, the reaction vessel is nickel or a nickel alloy and is either empty or packed with nickel or a nickel alloy, and the reaction time is between 0.2 and 8 minutes.

35 17. The process of Claim 1 wherein the reaction vessel is either an alloy containing about 76 percent nickel, about 15.5 percent chromium and about 8 percent iron or an alloy containing about 59

percent nickel, about 15.5 percent chromium, about 16 percent molybdenum and about 3.75 percent tungsten; 5 and wherein the reaction vessel either is empty or is packed with an alloy containing about 76 percent nickel, about 15.5 percent chromium and about 8 percent iron, or of an alloy containing about 59 percent nickel, about 15.5 percent chromium, about 16 percent molybdenum and about 3.75 percent tungsten. 10

18. The process of Claim 1 wherein n is 2 to 10; and wherein the hydrogenolysis is conducted in a reaction vessel of nickel, iron, cobalt, or their 15 alloys which either is empty or is packed with silicon carbide, or low surface area carbon, or with metal pipe, saddles, rings, perforated plates, wire, chips or shot of nickel, iron, cobalt or their alloys, at a temperature within the range of from 20 350°C to 700°C and for a time sufficient to provide conversion of said halocarbon and to produce as the major product of the conversion, hydrogenolysis product wherein at least one of X of the halocarbon has been replaced by a hydrogen atom.

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19. The process of Claim 18 wherein q is 2 to 22, and the major product of the conversion is hydrogenolysis product wherein just one X has been replaced by a hydrogen atom.

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20. The process of Claim 1 wherein n is 1, m is 0 to 1, p is 0 to 2, and q is 2 to 4; and wherein the hydrogenolysis is conducted at a temperature within the range of from 350°C to 700°C and for a 35 time sufficient to provide conversion of said halocarbon and to produce as the major product of the conversion, hydrogenolysis product wherein just one X has been replaced by a hydrogen atom.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 90/05637

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC⁵: C 07 C 17/00

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

Classification System	Classification Symbols
IPC ⁵	C 07 C 17/00

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched ⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	Chemical Abstracts, volume 111, no. 13, (Columbus, Ohio, US), Furutaka Yasuhisa et al.: "Preparation of 1,1,1,2-tetrafluoroethane", & JP, A, 0193549 (DAIKIN INDUSTRIES LTD.) 12 April 1989 ---	1-5,18,20
A	US, A, 2494064 (J.H. SIMONS et al.) 10 January 1950 -----	

* Special categories of cited documents: ¹⁰
 "A" document defining the general state of the art which is not
 considered to be of particular relevance
 "E" earlier document but published on or after the international
 filing date
 "L" document which may throw doubts on priority claim(s) or
 which is cited to establish the publication date of another
 citation or other special reason (as specified)
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 other means
 "P" document published prior to the international filing date but
 later than the priority date claimed

"T" later document published after the international filing date
 or priority date and not in conflict with the application but
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 invention
 "X" document of particular relevance; the claimed invention
 cannot be considered novel or cannot be considered to
 involve an inventive step
 "Y" document of particular relevance; the claimed invention
 cannot be considered to involve an inventive step when the
 document is combined with one or more other such docu-
 ments, such combination being obvious to a person skilled
 in the art.
 "A" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 24th January 1991	Date of Mailing of this International Search Report 18 FEB 1991
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer MISS T. TAZELAAR

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.

US 9005637
S4 41318

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 11/02/91. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 2494064		None	